Elevated iron to nitrogen recycling by mesozooplankton in the Northeast Atlantic Ocean

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[1] Low dissolved iron (DFe) concentrations limit primary production in most high-nutrient low-chlorophyll (HNLC) regions. Increased recycling of iron (Fe) relative to nitrogen (N) by zooplankton may help to sustain phytoplankton production in these conditions. We concurrently determined rates of DFe and ammonium (NH_4^+) recycling by natural mesozooplankton communities in HNLC conditions of the Northeast Atlantic. NH_4^+ excretion remained constant and ranged between 14.2–54.1 nmol NH_4^+ mg dry weight^{-1} h^{-1}. Fe recycling ranged between 6–138 pmol DFe mg dry weight^{-1} h^{-1} during the first hour and decreased thereafter, reflecting the transition from the loss of phytoplankton-derived Fe to basal DFe excretion. Mesozooplankton-driven nutrient recycling was estimated to support 6–59% and <1–13% of the respective phytoplankton requirements for DFe and N; DFe:N regeneration ratios were 5–26 times larger than those required by phytoplankton. Our data suggest that Fe recycling by grazing organisms has the potential to reduce the intensity of HNLC conditions. **Citation:** Giering, S. L. C., S. Steigenberger, E. P. Achterberg, R. Sanders, and D. J. Mayor (2012), Elevated iron to nitrogen recycling by mesozooplankton in the Northeast Atlantic Ocean, *Geophys. Res. Lett.*, *39*, L12608, doi:10.1029/2012GL051776.

1. Introduction

[2] Phytoplankton play a fundamental role in biogeochemical cycles, accounting for approximately 50% of global annual carbon fixation [*Field et al.*, 1998]. Their growth in large parts of the oceans is limited by a shortage of nutrient elements such as nitrogen (N), phosphate and iron (Fe). 'New production', based on nutrients that are introduced into the photic zone of the oceans via upwelling and atmospheric deposition, typically represents a relatively minor fraction of total production. Phytoplankton growth depends largely on nutrients that are recycled within the system [*Banse*, 1995]: This 'regenerated production' is often 6 times greater than that of new production [*Honjo et al.*, 2008].

[3] High-nutrient low-chlorophyll (HNLC) conditions are believed to arise due to the suboptimal supply ratios of Fe compared to N relative to the requirements for these elements by phytoplankton [*Boyd et al.*, 2007]. This may be exacerbated by the observed preferential recycling of N relative to Fe as material sinks indicated by increasing particulate Fe:N ratios with depth [*Frew et al.*, 2006]. However, if a significant fraction of the production is recycled in the upper ocean by processes that retain more Fe relative to N in the upper ocean, then this may act to alleviate the intensity of the HNLC condition.

[4] We hypothesise that mesozooplankton grazing may be such a process, as it returns relatively more of the ingested Fe (89–91% [*Schmidt et al.*, 1999]) than N (21–70% [*Vincent et al.*, 2007; *Mayor et al.*, 2011]) to the water column during recycling processes. This is supported by observations of dissolved Fe release (DFe; <0.2 μm size fraction) [*Schmidt et al.*, 1999; *Sarthou et al.*, 2008] during the consumption and digestion of their prey owing to the physical disruption of phytoplankton cells [*Frey and Small*, 1979] and possibly aided by their low gut pH of 5.4–6.7 [*Tang et al.*, 2011].

[5] Indeed, simultaneous measurements of total Fe and N release by krill in the Southern Ocean suggested zooplankton as an important node for Fe recycling [*Tovar-Sanchez et al.*, 2007]. However no studies that we are aware of have tested this hypothesis via the simultaneous measurement of DFe and N release by mesozooplankton during HNLC conditions in the North Atlantic Ocean. Here we report observations in the central high-latitude North Atlantic Ocean, which plays an important role in biological carbon sequestration, exporting 36–100 g C m^{-2} y^{-1} [*Sanders et al.*, 2005]. The modest residual nitrate pool in this region at the end of summer is suggestive of seasonal Fe limitation [*Sanders et al.*, 2005], which has been confirmed using shipboard bioassay experiments [*Nielsdóttir et al.*, 2009].

2. Methods

[6] Release rates of DFe and ammonium (NH_4^+) by mesozooplankton were investigated at five sites in July/August 2010 on board the RRS *Discovery* (cruise D354) in the Irminger Basin (Station R1), west and east of the Reykjanes Ridge (R3 and R4, respectively) and in the Iceland Basin (R5 and R6) (Figure 1 and Table 1). This cruise targeted the post spring bloom period when earlier observations suggested that HNLC conditions would be well established.

[7] All equipment was acid cleaned with 10% hydrochloric acid before use. Ambient seawater was collected using trace metal clean procedures and filtered using a 0.2-μm pore size filter capsule (Sartobran P300, Sartorius). Mesozooplankton were collected using a 200-μm, 1-m diameter WP2 net fitted with a non-filtering cod-end, hauled vertically from 20–30 m. All animals were immediately washed and briefly held in

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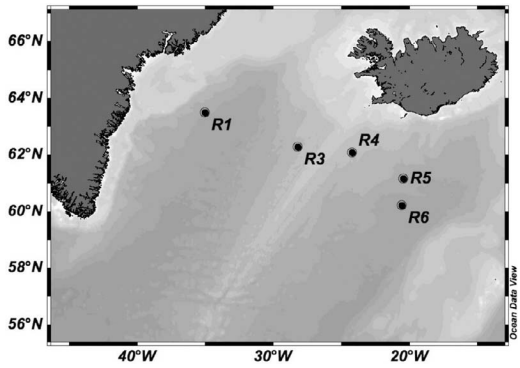

Figure 1. Stations where the release of DFe and NH_4^+ by mesozooplankton was determined.

0.2-μm filtered seawater (Table 1). Mesozooplankton were then transferred into 10 L of 0.2-μm filtered seawater and incubated for ≤5 h in a class 100 laminar flow hood in darkness at the ambient sea surface temperature of 12°C. No damaged or dead animals were observed during our incubation. However, we cannot exclude the possibility that some animals had been damaged and contributed to DFe and NH_4^+ release via the leakage of intracellular fluids. The densities of incubated mesozooplankton in the incubations ranged between 1.1–124.0 mg DW L^{-1} (Table 2). There was no correlation between density and individual NH_4^+ excretion rates ($R^2 = 0.04$, $p = 0.75$), in agreement with previous work [*Huntley and Nordhausen*, 1995]. We are thus confident that crowding did not significantly affect release rates.

[8] Samples for NH_4^+ (10 mL) analysis were collected before the introduction of experimental mesozooplankton (t_0) and thereafter 18 times at intervals of increasing length (5–60 min) with the last sample taken after 300 min. Samples for DFe (15 mL) analysis were collected at t_0 and 20, 40, 60, 120, 180 and 260 min after transfer. Samples were obtained using a peristaltic pump fitted with silicone tubing. No animals were removed during the sampling procedure. The samples for DFe were filtered using 0.2-μm membrane filters (polycarbonate 25 mm diameter, Whatman Nuclepore). All experiments were conducted using trace metal clean protocols following *Achterberg et al.* [2001].

[9] In parallel, a control incubation of filtered seawater was undertaken in which NH_4^+ concentrations were monitored over time. A small increase in NH_4^+ concentration was observed (3.3 ± 2.8% of the concentration increase observed in the experimental incubations) and our NH_4^+ release data was therefore corrected to reflect this. A similar suite of control experiments was not carried out for DFe release as it is well established that DFe concentrations in filtered seawater decrease over time [*Fischer et al.*, 2007] as DFe rapidly adsorbs to the walls of the incubation container. Our estimates of Fe release rates therefore represent lower limits for this biogeochemically important process. However, in future it would clearly be preferable to undertake a control.

[10] Samples for DFe were acidified (pH ~ 2) with nitric acid (Romil UpA) and analyzed on board following *Obata et al.* [1993]. The detection limit for this technique was 20 pM, with a precision of <5%. NH_4^+ in the release experiments was determined fluorometrically on ship using orthophthalate (OPA) following *Holmes et al.* [1999]. Samples for chlorophyll analysis (100–200 mL) were filtered using GF/F filters (Whatman) and then extracted in 90% acetone for 24 h in the dark before analysis with a fluorometer (TD70; Turner Designs) with *Welschmeyer* filters.

[11] Mesozooplankton from each experiment were preserved in 4% saline formaldehyde. On shore, preserved samples were counted, identified, and analysed for dry weight (DW). Copepods dominated at all stations, with large calanoids constituting 50.1–98.7% of the total biomass (Figure S1 in the auxiliary material).[1] Biomass values were corrected for a DW loss of 40% of fresh weight due to formaldehyde preservation (37–43% in mixed zooplankton [*Giguère et al.*, 1989]).

[12] The total volume of incubation water was reduced by sequential subsampling. The total quantity of NH_4^+ or DFe (*Fe*; nmol mg DW^{-1}) released by mesozooplankton per mg DW of biomass until time *t* was thus calculated as

$$Fe = Fe_{t-1} + V_{t-1} \times (c_t - c_{t-1}) \times B_{Incub}^{-1} \quad (1)$$

where *V* is the volume (L) of incubation water, *c* is the concentration (nM), and B_{Incub} is the total mesozooplankton biomass (mg DW) in the incubation container. The increase in NH_4^+ and DFe over time was fitted using linear regression and an exponential model with asymptote, respectively. The initial release rate (nmol mg DW^{-1} h^{-1}) was estimated from the models as total release after one hour. Basal DFe release rate was estimated as the rate 3 h after onset of starvation. Hourly release rates were extrapolated to daily rates using 24 h for NH_4^+ and 7 h initial release plus 17 h basal release for DFe. Values are presented ±s.d. All statistics were carried out in the R programming environment v. 2.10.0 [*R Development Core Team*, 2009].

3. Results and Discussion

[13] This study presents the first parallel NH_4^+ and DFe release rates by mesozooplankton communities in the North Atlantic Ocean. The observed NH_4^+ excretion rates of 14.2–

[1]Auxiliary materials are available in the HTML. doi:10.1029/2012GL051776.

Table 1. Details of the Five Stations Sampled[a]

Station	Date	Time (h:mm)	Position (N)	(W)	Water Depth (m)	Sampling Depth (m)	Chl (μg L^{-1})	*T* (min)	PP (mmol C m^{-3} d^{-1})	MZ Abundance (ind. m^{-3})	MZ Biomass (mg DW m^{-3})
R1	30 Jun	3:53	63.49.2	35.01.0	2124	20	0.81	11	2.3 ± 0.4	458.9	131.6
R3	1 Aug	3:40	62.28.4	28.21.2	1684	30	0.75	20	2.4 ± 0.1	53.9	9.5
R4	3 Aug	5:00	62.08.1	24.19.1	1376	30	0.82	25	3.1 ± 0.2	29.5	7.0
R5	4 Aug	4:05	61.15.6	20.42.3	2229	30	0.85	35	2.7 ± 0.1	11.3	0.8
R6	7 Aug	3:40	60.21.6	20.56.7	2661	30	0.74	20	2.6[b] ± 0.4	10.3	0.9

[a]MZ: mesozooplankton, Chl: average chlorophyll *a* concentration; *T*: the time between net retrieval and incubation.
[b]Based on average values.

Table 2. Mesozooplankton Release Rates, Phytoplankton Uptake Rates, and Release-to-Uptake Ratios for N and Fe During Our Study[a]

Station	Density During Incubation (mg DW L^{-1})	NH_4^+ Release (nmol N mg DW^{-1} h^{-1})	NH_4^+ Release (μmol N m^{-3} d^{-1})	DFe Release Basal (pmol DFe mg DW^{-1} h^{-1})	DFe Release Digestion-Derived (pmol DFe mg DW^{-1} h^{-1})	DFe Release (nmol DFe m^{-3} d^{-1})[b]	Uptake (mmol N m^{-3} d^{-1})	Uptake (nmol Fe m^{-3} d^{-1})	Release/Uptake (% N)	Release/Uptake (% Fe)
R1	124.0	14.2	44.8	0.001	6.3	5.8	0.3	9.9	12.9	58.7
R3	13.4	17.5	4.0	0.7	21.7	1.6	0.4	10.3	1.1	15.1
R4	9.9	16.0	2.7	-	-	-	0.5	13.3	0.6	-
R5	1.1	46.9	0.9	9.7	107.5	0.7	0.4	11.3	0.2	6.3
R6	1.3	54.1	1.2	12.3	138.1	1.1	0.4	11.2	0.3	9.5

[a]Uptake rates are stoichiometrically obtained from primary production data.
[b]Daily Fe release rates are based on 7 h digestion and 17 h basal excretion.

54.1 nmol NH_4^+ mg DW^{-1} h^{-1} (Table 2) are in good agreement with previous estimates derived from boreal copepods (1.5–50 nmol NH_4^+ mg DW^{-1} h^{-1} [*Ikeda et al.*, 2001]) and from a mixed zooplankton community (0.1–65.2 nmol NH_4^+ mg DW^{-1} h^{-1} [*Ikeda et al.*, 2000]). Our estimates of basal and digestion-derived release rates of DFe varied between <0.01–12 and 6–138 pmol DFe mg DW^{-1} h^{-1}, respectively (Table 2). Daily release estimates ranged from 0.04–1.18 nmol DFe mg DW^{-1} d^{-1}, the same order of magnitude as reported for Antarctic krill, *Euphausia superba* (0.04–0.17 nmol DFe mg DW^{-1} d^{-1} [*Schmidt et al.*, 2011]). *Sarthou et al.* [2008] presented shipboard measurements of DFe recycling by copepods incubated in seawater containing radiolabelled phytoplankton. Assuming that regenerated Fe equals the sum of Fe uptake and the increase in DFe at the end of their incubation, copepods regenerated 0.004–0.019 nmol DFe mg DW^{-1} d^{-1} [*Sarthou et al.*, 2008]. These values are an order of magnitude smaller than our estimates, possibly reflecting that their budget calculations do not account for continuous recycling. *Tovar-Sanchez et al.* [2007] observed release rates of 0.5–17 nmol Fe mg DW^{-1} d^{-1} by krill in the Southern Ocean. These rates included the production of both DFe and acid-leachable particulate Fe, possibly explaining why they are more than an order of magnitude greater than our observations and those of *Schmidt et al.* [2011].

3.1. Controls Over NH_4^+ and DFe Release

[14] The increase of DFe and NH_4^+ concentrations in the incubations over time followed different trends indicating fundamentally different release pathways. The near constant increase in NH_4^+ concentrations during our incubations (Figure 2a) reflects the accumulation of excretory waste products; crustacean zooplankton catabolise nitrogenous products and thus excrete NH_4^+ even during starvation [*Mayor et al.*, 2011]. Previous starvation incubations studies, conducted over several days, have reported NH_4^+ excretion rates to decline over time [*Atkinson and Whitehouse*, 2001]. This effect was not apparent in our short (<5 h) incubation experiments; mesozooplankton excretion rates have been shown to be fairly constant during the initial hours of starvation [*Huntley and Nordhausen*, 1995].

[15] In contrast, DFe concentrations increased rapidly during the first half hour, and the release rate slowed down thereafter and became negligible after ~2 h (Figure 2b). This likely reflects the initial, rapid increase of DFe being caused by the elimination of phytoplankton-derived Fe from zooplankton guts. Previous work has demonstrated that an increase of DFe concentrations during zooplankton grazing originates from phytoplankton cells [*Hutchins et al.*, 1995], with the rate of increase being consistent with the removal of chlorophyll or radiolabelled Fe from zooplankton guts [*Wang and Dei*, 2001]. We suggest that the apparent decline in the rate at which DFe accumulated in our incubations reflects the transition from digestion-derived DFe release towards basal DFe excretion.

[16] The observed biomass-specific release rates of NH_4^+ and DFe differed considerably between stations. A previous study suggested a positive relationship between Fe release by *E. superba* and ambient chlorophyll concentrations [*Tovar-Sanchez et al.*, 2007]. We did not find a relationship between ambient chlorophyll concentrations and the release of either NH_4^+ or DFe ($R^2 \leq 0.01$, $p \geq 0.85$ in both cases), reflecting the relatively constant concentrations of chlorophyll across all stations (Table 1). Proximity to hydrothermal

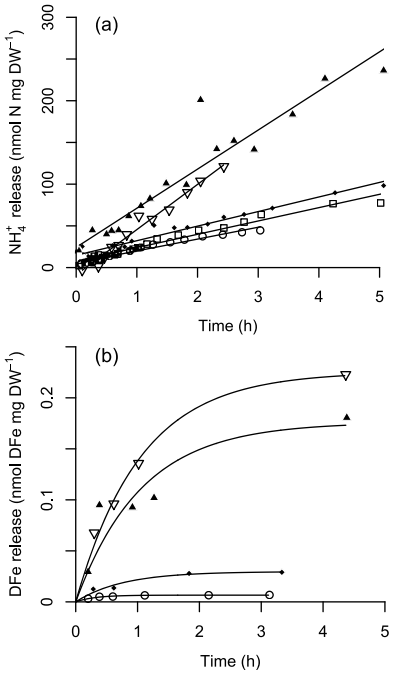

Figure 2. Release over time of (a) NH_4^+ and (b) DFe during incubations at stations R1 (circle), R3 (diamond), R4 (square), R5 (triangle), and R6 (inverted triangle). Lines represent linear regression for NH_4^+ (in order R^2 = 0.97, 0.95, 0.96, 0.90 and 0.98; $p < 0.01$ for all stations) and an exponential fit with asymptote for DFe (in order R^2 = 0.96, 0.92, 0.80 and 0.99; $p \leq 0.01$, 0.08, 0.09 and 0.01), respectively (Table S1).

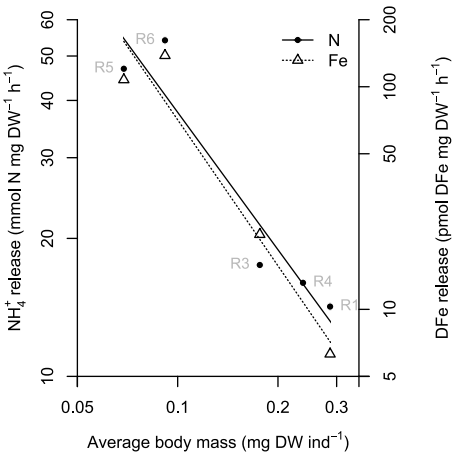

Figure 3. Relationship between average body mass and release of NH_4^+ (circles) and DFe (triangles) during the first hour at stations R1–R6. Linear regressions: $\log(N) = -0.97 \cdot \log(DW) + 1.34$ ($p = 0.01$, $R^2 = 0.91$) and $\log(DFe) = -2.18 \cdot \log(DW)$ ($p = 0.03$, $R^2 = 0.94$).

vents has also been reported to influence the release rate of trace metals by zooplankton [*Tovar-Sanchez et al.*, 2009]. The distances between sampling depth and sea floor (Table 1) were sufficiently large in our study to prevent any potential hydrothermal vent plume enhancing the trace metal release by surface feeding mesozooplankton [*Lupton*, 1995].

[17] Rather, we suggest that the variability of release rates between stations reflects the relationship between animal size and metabolism. Biomass-specific NH_4^+ excretion rates decrease with increasing body size, as small zooplankton have a higher metabolic rate per unit body weight compared to larger zooplankton [*Conover and Corner*, 1968]. Indeed, average body mass explained 91 and 94% of the variability in NH_4^+ and DFe release rates respectively during the first hour (Figure 3). The size-dependent release of DFe can thus be attributed to the relationship between animal size and metabolism, which causes weight-specific ingestion rates to decrease with increasing body mass [*Hansen et al.*, 1997]: less food intake per unit biomass subsequently leads to lower solubilisation and biomass-specific release of DFe from ingested phytoplankton.

3.2. Potential Support for Primary Production

[18] Here we present the first attempt to quantify the importance of Fe recycling by mesozooplankton on primary production in the high-latitude North Atlantic. Phytoplankton nutrient uptake was estimated by converting primary production data (measured using a ^{14}C technique (Poulton, unpublished data, XXXX) as described by *Poulton et al.* [2010]) to N and Fe uptake using a C:N ratio of 106:16 mol mol^{-1} and a Fe:C ratio of 4.3 μmol mol^{-1} (s.d. $\pm$ 1.5; measured during the cruise (C. M. Moore, unpublished data, 2012)). The latter compares well to literature values for temperate, Fe-limited taxa (2–10 μmol mol^{-1}) [*Sunda and Huntsman*, 1995].

[19] It is not possible to determine whether DFe was solubilised in the guts and (1) directly released into ambient water or (2) incorporated into fecal material from which DFe leached by diffusion after egestion. The latter pathway could cause significant amounts of DFe to sink out to deep waters, where it becomes unavailable to phytoplankton. We observed that most DFe was released during the initial 2 h of our incubation. As average sinking speed of copepod fecal pellets is <10 m h^{-1} (review by *Turner* [2002]), DFe was likely released <20 m below the depth of egestion and thus available to of phytoplankton.

[20] Assuming the products released by mesozooplankton were bioavailable and representative of the region, mesozooplankton-derived NH_4^+ therefore had the potential to support 3.0 $\pm$ 5.5% (0.2–12.9%) of the N uptake by primary production (Table 2). This is in good agreement with the estimate of 3.9% in the North Atlantic region between 60–80°N [*Hernández-León et al.*, 2008]. Fe recycling appeared to be more important, with the potential to support 22.4 $\pm$ 24.5% (6.3–58.7%) of the daily requirements for primary production across the region of study (Table 2). Sources of uncertainty for the latter estimate are potential variability of community composition and thus phytoplankton Fe:C ratios. The community showed little variation across the study sites and was dominated by small (<5 μm) flagellates (A. J. Poulton, unpublished data, 2012). Using the above mentioned Fe:C ratios of 2 and 10 μmol mol^{-1} as upper and lower limit, relative support ranged from 10 $\pm$ 11% to 48 $\pm$ 53%.

[21] The utilization of Fe sources by phytoplankton depends on factors such as lability of DFe and species of Fe-binding ligands [e.g., *Hutchins et al.*, 1999], hence not all released DFe may contribute to primary production. Conversely, there is evidence that a significant fraction of particulate Fe may become available to phytoplankton via, e.g., ligand-assisted dissolution and photochemical processes [*Lippiatt et al.*, 2010, and references herein]; a possible source of Fe that we have not accounted for in this study.

[22] It is noteworthy that the site where mesozooplankton-mediated NH_4^+ and DFe recycling was most important also showed the highest mesozooplankton abundance. This suggests that areas experiencing heavy grazing pressure due to high mesozooplankton abundance, as being the case in the Irminger Basin [*Gislason et al.*, 2008], are sites of extensive nutrient recycling.

[23] The DFe:N regeneration ratios ranged between 129–745 μmol mol^{-1} and were 5–26 times larger than the calculated Fe:N ratios in phytoplankton (42.4 μmol mol^{-1}). This regeneration ratio is possibly a slight overestimate as it does not include the release of urea and amines, although their release is reported to occur in relatively small amounts (14–26% of total N excreted) [*Miller and Roman*, 2008]. The high DFe:N regeneration ratio is consistent with copepod physiology: copepods absorb 60–79% of ingested N [*Vincent et al.*, 2007; *Mayor et al.*, 2011] and only 5–16% of ingested Fe [*Wang and Dei*, 2001]. This suggests that mesozooplankton recycle Fe into the dissolved phase much faster than N, a decoupling that results in considerably more Fe being available to support primary production than would be predicted from a simple consideration of Fe:N ratios in the upper ocean and an estimate of Fe supply.

[24] Relatively high Fe:N ratios observed in sinking particulate matter [*Frew et al.*, 2006], including copepod fecal pellets, suggest that mesozooplankton defecation drives pelagic ecosystems towards Fe limitation. The notion that mesozooplankton rapidly recycle, and thus retain DFe in surface waters is at odds with this interpretation. However, it is strongly supported by the observation that the copepods release ~50% of ingested Fe into the dissolved phase and only ~30% as particulate matter [*Schmidt et al.*, 1999]. Our

study clearly highlights the need for a better understanding of the role of mesozooplankton in nutrient recycling, particularly with regards to the relative partitioning of Fe and N into the dissolved and particulate phases; this has important implications for the role that Fe plays relative to N in regulating marine primary production.

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